

UNITED STATES PATENT APPLICATION
FOR
CLEANING PROCESSES FOR SILICON CARBIDE MATERIALS

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CLEANING PROCESSES FOR SILICON CARBIDE MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

This invention is related to U.S. Patent Application No. 10/627,416 (Attorney Reference No. 59081-8007.US01) entitled "ULTRASONIC ASSISTED ETCH USING CORROSIVE LIQUIDS" filed by Samantha S. H. Tan on July 24, 2003, the content of which is incorporated herein by reference. This invention is also related to U.S. Patent Application No. 10/627,185 (Attorney Reference No. 59081-8009.US01) entitled "CLEANING PROCESS AND APPARATUS FOR SILICATE MATERIALS" filed by Samantha S. H. Tan and Ning Chen on July 24, 2003, the content of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to cleaning processes and, more specifically, to cleaning processes for silicon carbide materials.

BACKGROUND OF THE INVENTION

Several forms of silicon carbide materials are used in the manufacture of semi-conductor wafers. For example, hollow silicon carbide pins are used as wafer-lift pins. Silicon carbide rings are used as wafer-rings for holding e-chucks. Silicon carbide wafer-showerheads are used in cleaning semi-conductor wafers. However, such materials are required to be ultra-clean in order not to contaminate the semi-conductor wafers. The silicon carbide wafer-lift pins, wafer-rings and wafer-showerheads can be made either by a sintering process or by chemical vapor deposition (CVD). While sintered silicon carbide materials are less expensive, they possess more impurities, and thus require more cleaning than CVD silicon carbide materials.

FIG. 1A is a simplified longitudinal cross-sectional view of a hollow silicon carbide wafer-lift pin 100 with plenum 104. Both the exterior surface of the silicon carbide wafer-lift pin as well as the interior surface of the silicon carbide wafer-lift pin needs to be cleaned before such pins are used in the manufacture of semiconductor wafers. Thus, exterior surface 105 and interior surface 106 of silicon carbide wafer-lift pin 100 need to be cleaned to a high degree of purity.

FIG. 1B is a simplified drawing illustrating a plan view 110 of a silicon carbide wafer-ring 112. Arrows A-A indicate the direction of the cross-sectional view of wafer-ring 112 as illustrated in FIG. 1C. In FIG. 1B, the recessed portion 114 represents a lowered lip 114 at the inner diameter of the wafer-ring. Lip 114 aids in holding an e-chuck as described with reference to FIG. 1C.

FIG. 1C a simplified drawing illustrating a cross-sectional view 120 of the wafer-ring of FIG. 1B taken in the direction A-A as shown in FIG. 1B. In FIG. 1C, wafer-ring 124, fits over e-chuck 122. Lip 126 of wafer-ring 124 helps hold the e-chuck in place.

FIG. 1D is a simplified longitudinal cross-sectional view 150 of a wafer-showerhead 154. In this case, wafer-showerhead 154 is bonded to an anodized aluminum base 155. There exists a plenum 152 between the anodized aluminum base 155 and wafer-showerhead 154 as indicated in FIG. 1D. The wafer-showerhead 154 is perforated allowing any fluid that is present in the plenum region to pass to the exterior of the wafer-showerhead.

Based on the foregoing, there is a need for cleaning silicon carbide materials to achieve high purity materials.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings and in which like reference numerals refer to similar elements and in which:

5 FIG. 1A is a simplified longitudinal cross-sectional view of a hollow silicon carbide wafer-lift pin 100;

FIG. 1B is a simplified drawing illustrating a plan view 110 of a silicon carbide wafer-ring;

10 FIG. 1C is a simplified drawing illustrating a cross-sectional view 120 of the wafer-ring of FIG. 1B;

FIG. 1D is a simplified longitudinal cross-sectional view 150 of a wafer-showerhead;

FIG. 2 is a flowchart illustrating some steps in a method for cleaning silicon carbide materials;

15 FIG. 3 is a simplified drawing illustrating a wafer boat 300 adapted for cleaning a multiplicity of silicon carbide wafer-rings;

FIG. 4A is a simplified schematic illustrating a pin rack 400 for holding a multiplicity of silicon carbide wafer-lift pins, according to certain embodiments of the invention;

20 FIG. 4B is a plan view of top portion of the pin rack of FIG. 4A;

FIG. 5 is a simplified schematic illustrating a set-up for cleaning silicon carbide wafer-lift pins, according to certain embodiments of the invention; and

25 FIG. 6 is a simplified schematic illustrating a set-up adapted for cleaning a fixtured silicon carbide wafer-showerhead, according to certain embodiments of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The cleaning of silicon carbide materials on a large scale is described. In the following description, for purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art that the present invention may be practiced without these specific details. In other instances, well-known structures and devices are shown in block diagram form in order to avoid unnecessarily obscuring the present invention.

CLEANING PROCESSES

FIG. 2 is a flowchart that illustrates some steps in a method 200 for cleaning of silicon carbide materials, according to certain embodiments of the invention. Method 200 starts at operation 202 and proceeds to operation 204. Silicon carbide materials, such as silicon carbide wafer-lift pins, wafer-rings and wafer-showerheads are obtained at operation 204.

At operation 206, a decision is made as to whether the silicon carbide material is sintered. If the silicon carbide material is not sintered, then method 200 proceeds to operation 208 where the silicon carbide material undergoes ultrasonic assisted etching (UAE) in an aqueous acid solution. Various techniques may be used to perform UAE on the silicon carbide material. The techniques may vary from implementation to implementation. One such technique is described in U.S. Patent Application No. 10/627,416 (Attorney Reference No. 59081-8007.US01) entitled "ULTRASONIC ASSISTED ETCH USING CORROSIVE LIQUIDS" filed by Samantha S. H. Tan on July 24, 2003, the content of which is incorporated herein by reference.

According to certain embodiments, at operation 208, the silicon carbide material undergoes UAE by ultrasonication in an aqueous acid solution that

includes water (H₂O) and acids such as hydrofluoric acid (HF) and nitric acid (HNO₃). Such an aqueous solution may be made up of 5% - 20% wt. HF, 20% - 95% wt. HNO₃, and 0% - 80% wt. H₂O. The UAE operation is performed for about 10 to 15 minutes at about room temperature to about 50°C. The ultrasonication is 5 performed at a frequency of about 25 kHz to about 40 kHz and at a power of about 30 watts/gal to about 50 watts/gal.

Next, at operation 210 a decision is made as to whether the silicon carbide material is a wafer-lift pin. If the silicon carbide material is a wafer-lift pin, then the wafer-lift pin is cleaned for about 30 minutes to about an hour in an aqueous acid 10 solution using a pump at operation 212. A multiplicity of wafer-lift pins may be cleaned simultaneously by using a pin rack. The pin rack is described in further detail herein with reference to FIG. 4A and 4B. Operation 212 is described in greater detail herein with reference to FIG. 5. Throughout method 200, a multiplicity 15 of silicon carbide wafer-rings can be cleaned simultaneously by placing multiple silicon carbide wafer-rings in a wafer boat. Such a wafer boat is described in further detail herein with reference to FIG. 3.

If the silicon carbide material is not a wafer-lift pin, then at operation 214, the silicon carbide material is ultrasonicated in a bath of deionized water. Various techniques may be used to perform the ultrasonication in deionized water of the 20 silicon carbide material. The techniques may vary from implementation to implementation. One such technique is described in U.S. Patent Application No. 10/627,185 (Attorney Reference No. 59081-8009.US01) entitled "CLEANING PROCESS AND APPARATUS FOR SILICATE MATERIALS" filed by Samantha S. H. Tan and Ning Chen on July 24, 2003, the content of which is incorporated herein 25 by reference. According to certain embodiments, at operation 214, the silicon carbide material undergoes ultrasonication in a bath of deionized water for about 30

minutes to about 60 minutes. The temperature may range from about room temperature to about 50°C. The ultrasonication is performed at a frequency of about 25 kHz to about 40 kHz and at a power of about 30 watts/gal to about 50 watts/gal at about 80-90% power intensity.

5 The method 200 then proceeds to operation 216 where the silicon carbide material makes contact with a dilute solution that includes hydrofluoric acid, hydrogen peroxide (H₂O₂) and nitric acid. Such a dilute solution may be made up of 0.5% - 1.5% wt. HF, 1% - 10% wt. H₂O₂, and 0.1% - 0.5% wt. HNO₃, according to certain embodiments. According to other embodiments, such a dilute solution may
10 be made up of 0.1% - 5.0% wt. HF, 0.1% - 20.0% wt. H₂O₂, and 0.1% - 5.0% wt. HNO₃. The silicon carbide material makes contact with the dilute solution of HF:H₂O₂:HNO₃ for about 5 minutes to about 15 minutes at about room temperature.

Next, the method 200 proceeds to operation 218 where the silicon carbide material is baked at a temperature of about 200°C to about 300°C. Silicon carbide wafer-rings and wafer-lift pins are baked for about 2 hours to about 3 hours. Silicon carbide wafer-showerheads with fixtures are baked for about 6 hours to about 24 hours. The baking in operation 218 may be performed in either a convection oven, a nitrogen-purge oven, or a vacuum oven located in a class 1000 clean room. Further, according to certain embodiments, heat lamps may be used if moisture
15 content is not a critical consideration. Method 200 then terminates at operation 220.

20 Referring back to operation 206, if the silicon carbide material is determined to be sintered, then method 200 proceeds to operation 222. At operation 222, a decision is made as to whether the sintered silicon carbide material is bonded to
25 another material.

If the sintered silicon carbide material is not bonded, then a decision is made at operation 224 as to whether the sintered silicon carbide material needs to meet a high purity requirement.

If the sintered silicon carbide material is to meet a high purity requirement,

5 then the silicon carbide material is oxidized at a high temperature in operation 226. According to certain embodiments, the sintered silicon carbide material is oxidized at a temperature of about 1000°C to about 1200°C. According to certain other embodiments, the sintered silicon carbide material is oxidized at a temperature of about 800°C to about 1500°C. The oxidation converts the impurities in the silicon carbide material to oxides. Such oxides may then be removed by UAE at operation 10 228. The UAE operation is similar to the one described herein with reference to operation 208.

Method 200 then proceeds to operation 230 where the sintered silicon carbide material is scrubbed to remove impurities. For example, the sintered silicon carbide material may be scrubbed using a nylon brush.

15 At operation 232, a decision is made as to whether the sintered silicon carbide material has an unacceptable amount of residue. According to certain embodiments, the sintered silicon carbide material may be wiped using an acetone isopropyl alcohol wipe. The acetone isopropyl alcohol wipe is then visually 20 inspected for residue. If an unacceptable amount of residue is present, then operations 228 and 230 are repeated until the amount of residue is acceptable. According to certain other embodiments, the amount of residue may be determined using an appropriate analyzer. If at operation 232, it is decided that the amount of residue is acceptable, then method 200 proceeds to operation 214, which is 25 previously described herein.

Referring back to operation 222, if it is decided that the sintered silicon carbide material is bonded to another material, then the bonded/sintered silicon carbide material is fixtured at operation 234. For example, a silicon carbide wafer-showerhead may be bonded to an anodized aluminum base. In such a case, a 5 chemically resistant fixture may be attached to the anodized aluminum base by means of screws in order to prevent the anodized aluminum base from chemically reacting with any of the chemicals used during the cleaning processes as outlined by method 200. The fixture and screws are made of a chemically resistant material such as polyethylene, according to certain embodiments of the invention. The type 10 of chemically resistant material may vary from implementation to implementation.

Next, at operation 236, the fixtured silicon carbide material is purged with nitrogen gas at about 10 psi to about 20 psi pressure. The nitrogen gas purge continues until the final cleaning operation of the bonded and sintered silicon carbide material is complete. The nitrogen gas purge prevents migration of 15 chemicals, due to capillary action, from the various chemical baths in method 200 to the anodized aluminum base of the wafer-showerhead, for example. The cleaning process of a fixtured wafer-showerhead is explained in further detail with reference to FIG. 6 herein.

Next, at operation 238, a decision is made as to whether the fixtured silicon 20 carbide material is new. If the fixtured silicon carbide material is not new, i.e., it is recycled, for example, then the fixtured silicon carbide material undergoes a UAE operation at operation 242. The UAE operation is similar to the one described herein with reference to operation 208. From operation 242, the method 200 proceeds to operation 214, which is previously described herein.

25 If it is decided that the fixtured silicon carbide material is new, then the method 200 proceeds to operation 240 where the fixtured silicon carbide material is

soaked in an aqueous solution of HF:HNO₃:H₂O. Such an aqueous solution may be made up of 5% - 20% wt. HF, 20% - 95% wt. HNO₃, and 0% -80% wt. H₂O. The fixtured silicon carbide material is soaked in the HF:HNO₃:H₂O aqueous solution at about room temperature. After soaking the fixtured silicon carbide material, method 5 200 proceeds to operation 214, which is previously described herein.

WAFER BOAT

FIG. 3 is a simplified drawing illustrating a wafer boat 300 adapted for cleaning a multiplicity of silicon carbide wafer-rings. Wafer boat 300 includes several slots, with each slot adapted to hold a wafer-ring. Thus, wafer boat 300 can 10 hold several wafer-rings 304 such that several wafer-rings can be cleaned simultaneously. Wafer boat 300 includes handles 308a and 308b for convenient handling.

PIN RACK

FIG. 4A is a simplified schematic illustrating a pin rack 400 for holding a 15 multiplicity of silicon carbide wafer-lift pins, according to certain embodiments of the invention. Pin rack 400 includes a top portion 450 and a bottom portion 408. Wafer-lift pins 406 are inserted through the top portion 450 and extend to the bottom portion 408 with the pin heads 402 at the bottom. Top portion 450 is further described with reference to FIG. 4B.

20 FIG 4B is a plan view of top portion 450 of pin rack of FIG. 4A. Top portion 450 is a perforated plate with perforations 452. A wafer-lift pin may be inserted in each perforation to extend to the bottom portion of the pin rack.

SET-UP FOR CLEANING WAFER-LIFT PINS

FIG. 5 is a simplified schematic illustrating a set-up for cleaning silicon carbide wafer-lift pins, according to certain embodiments of the invention. In FIG. 5, the set-up 500 includes the following, according to certain embodiments:

- 5 1) a reservoir 510 that contains an aqueous solution 512 of HF, HNO₃, and H₂O;
- 2) a pump 508, which can be a peristaltic pump;
- 3) a manifold 506 attached to pump 508, which manifold delivers aqueous solution 512 to the wafer-lift pins;
- 10 4) a pin rack 504 for holding wafer-lift pins 502;
- 5) a tank 516 for catching any overflow of aqueous solution 512; and
- 6) a return hose 514 connecting tank 516 to reservoir 510.

In FIG. 5, wafer-lift pins 502 are oriented on pin rack 504 such that pin heads 503 are at the bottom of the pin rack. Pump 508 pumps aqueous solution 512 from 15 reservoir 510 through the manifold such that aqueous solution 512 fills the plenum of each wafer-lift pin to overflowing capacity. The overflow of aqueous solution 512 is collected at tank 516 and returned by return hose 514 to reservoir 510. To prevent contamination, reservoir 510, pump 508, manifold 506, pin rack 504, tank 516, and return hose 514 are all made of chemically resistant materials. One 20 example of a chemically resistant material is polyethylene.

FIXTURED WAFER-SHOWERHEADS

FIG. 6 is a simplified schematic illustrating a set-up adapted for cleaning a fixtured silicon carbide wafer-showerhead, according to certain embodiments of the invention. Set-up 600 of FIG. 6 includes the following, according to certain 25 embodiments:

- a) a tank 614;

- b) an aqueous solution 616 in tank 614;
- c) a wafer-showerhead 620;
- d) an anodized aluminum base 602 that is bonded to wafer-showerhead 620;
- e) fixture 604 that is secured to anodized aluminum base 602 via screws

5 606a and 606b;

- f) an O-ring 608; and

g) a flow of nitrogen gas 612 for purging the wafer-showerhead 620 and anodized aluminum base 602 through plenum 610.

To prevent contamination, fixture 604 is needed to cover the anodized

10 aluminum base 602 to prevent a chemical reaction between the anodized aluminum base 602 and aqueous solution 616. O-ring 608 provides a seal between fixture 604 and the anodized aluminum base 602. Fixture 604 and screws 606a and 606b are made of a chemically resistant material. The type of chemically resistant material may vary from implementation to implementation. According to certain 15 embodiments, polyethylene may be used. Nitrogen gas stream 612 is used as a purge in order to prevent migration of aqueous solution 616 up to anodized aluminum base 602 through capillary action.

In the foregoing specification, embodiments of the invention have been described with reference to numerous specific details that may vary from 20 implementation to implementation. Thus, the sole and exclusive indicator of what is the invention, and is intended by the applicants to be the invention, is the set of claims that issue from this application, in the specific form in which such claims issue, including any subsequent correction. Any express definitions set forth herein for terms contained in such claims shall govern the meaning of such terms as used 25 in the claims. Hence, no limitation, element, property, feature, advantage or attribute that is not expressly recited in a claim should limit the scope of such claim

in any way. The specification and drawings are, accordingly, to be regarded in an illustrative rather than a restrictive sense.
